Photocatalytic detoxification of aqueous organophosphorus by TiO_2 immobilized silica gel

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ARTICLE INFO

ABSTRACT

Photocatalytic degradation of organophosphorus compounds including organophosphonic and organophosphinic acids by TiO_2 immobilized silica gel in a water phase was carried out. Photocatalytic degradation of parent organophosphorus compounds and formation of intermediates were observed and the photocatalytic degradation scheme for each pesticide is proposed. Overall, the photocatalytic degradation of organophosphorus compounds in aqueous phase was estimated to form organophosphoric (organophosphonic and organophosphinic) acids as intermediates of the reaction. These organophosphoric acid intermediates were selectively adsorbed onto TiO_2 surface and as a result, elution of these compounds into the aqueous phase was not observed. Similarly, after photocatalytic degradation, H_3PO_4 was either not observed or slightly observed as the final product. Likewise, rapid adsorption of the studied parent organophosphoric acids on TiO_2 surface resulted in significant reduction in the concentration of these compounds even under dark condition. Upon UV irradiation, total organic carbon (TOC) level increased, and this is indicating the elution of some organic intermediates into the aqueous phase. However, these organic intermediates were eventually degraded with the UV irradiation.

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1. Introduction

In many developing countries, the use of pesticides is indispensable for the improvement of agricultural productivity. On the other hand, the problem of the residue-prone agricultural chemicals remains a major concern until today. One solution to this problem is the photocatalytic degradation of pesticides that has already 30 years history [1–4]. Until now, many studies for photocatalytic degradation of organic compounds including pesticides have been carried out, and the mechanism of purification by photocatalysis have been analyzed and described. In particular, the group of Herrmann et al. actively studied the photodegradation of organic compounds from early stage of photocatalyst research history, leading to significant contributions in this field [5–10]. Apart from the photodegradation of pesticides in the aqueous phase, Herrmann et al. have also worked on the application of solar light as source of energy in the photocatalytic process [11–17]. However, the formation of toxic organophosphorus intermediates during photocatalysis of organophosphorus pesticides remains to be a major problem that need to be addressed. For example,

hydrolysis of Acephate, a relatively mild insecticide, forms highly toxic Methamidophos as an intermediate [18]. Similarly, another insecticide, Dimethoate was found to generate a toxic intermediate Omethoate by hydrolysis [19]. Thus, there is a need to ensure that photocatalytic water purification systems do not result in the generation of hazardous intermediates, and that such systems will be practicable in real application. There have been many published reports on the photocatalytic degradation of organophosphorus pesticides. Nonetheless, most of such studies simply describe the photodegradation of the pesticides; no one mentioned about what particular kind of photocatalytic method is suitable for the total elimination of these compounds from aqueous phase.

It is well known that organophosphorus compounds and H_3PO_4 are easily adsorbed onto solid surfaces [20–29], particularly, TiO_2 [30–36]. Thus, it is expected that the treatment of organophosphorus compounds in an aqueous phase by photocatalyst is safe as organophosphoric acid intermediates such as organophosphonic (one P—C bond) or organophosphinic (two P—C bond) acid strongly adsorb onto TiO_2 surface and are not eluted to aqueous phase during photocatalytic decomposition [37]. It is speculated that the collision of TiO_2 nanoparticles with each other during mechanical stirring leads to desorption of the adsorbed H_3PO_4 from the TiO_2 surface. Hence, to avoid the elution of phosphorous intermediates and final products into the aqueous solution and also

to eliminate the need to filter out the photocatalyst after treatment [38], immobilized TiO$_2$ photocatalyst was used in this study. Using such system, the photocatalytic degradation of the parent organophosphorus compounds and the formation of intermediates and final products were observed. The photocatalytic degradation scheme of the organophosphorus compounds was also elucidated based on the experimental results. Overall, this study shows the possibility of purifying or detoxifying contaminated water through photocatalysis.

2. Experimental

2.1. Organophosphorus compounds

Organophosphorus compounds used in this experiment are shown in Table 1. All the organophosphorus compounds were purchased from Wako Chemicals as chemicals for pesticide residue analysis except for Glufosinate ammonium salt (Kanto Kagaku, for pesticide residue analysis). The reason to select these organophosphorus compounds is as follows: 1. water solubility, 2. relative stability at neutral to acidic pH close to natural environment, 3. mainly general pesticides (except for DMMP for simulant of chemical warfare). Concentration of organophosphorus compounds and the formation of intermediates were monitored by HPLC and IC. Some of organophosphorus compounds (DDVP, Monocrotophos, ESP, and DMMP) were difficult to observe by HPLC and IC, therefore we did not determine their quantity. The instruments that were used to analyze these organophosphorus compounds are also shown in Table 1.

Two hundred (200) mg/L of aqueous solutions of each organophosphorus compound was prepared as stock solution. The stock solutions were diluted 10 times to obtain around 1×10^{-4} mol/L of the organophosphorus chemical solutions that were used in the study. Standard solutions were also prepared from the respective stock solutions. Detailed concentrations of the solutions are shown in Table 1.

2.2. Experimental apparatus and photocatalyst

The photocatalyst consisted of 14 g of TiO$_2$ coated on silica gel (HQC21: Shinto V Cerax [39,40] (average diameter = 4 mm, average amount of TiO$_2$ = 20 wt%, specific surface area = 200 m^2/g, crystalline structure = anatase) that was packed into a spiral type Pyrex glass tube (external diameter = 12 mmØ, internal diameter = 10 mmØ) photocatalytic reactor. The circulation type photocatalytic reactor that was used in this study is shown in Fig. 1. Sample solution was introduced into a 200 mL reservoir and circulated through the system at 30 mL/min by a diaphragm pump (PZD-31-VFC-HWJ, Takumina). All of the piping used in the system consisted of PTFE tube (external diameter = 6 mmØ, internal diameter = 4 mmØ). A black light bulb (6 W, Toshiba: λ_{max} = 352 nm) that was used as the UV light source was placed into the center of the spiral reactor. The spiral reactor was covered by aluminum-deposited styrene foam sheet to reflect back UV light into the spiral reactor.

2.3. Experimental procedure and analytical instruments

The quantitative determination of Acephate, Methamidophos, Dimethoate, Omethoate, IBP, Glyphosate, and AMPA was carried out using HPLC (Hitachi LaChrom ELITE with L-2485 fluorescent detector or L-2455 diode array detector). Acephate, Methamidophos, Dimethoate, and Omethoate were analyzed using L-2455 diode array detector and Wakosil-II 5C18 RS (4.6 × 150 mm) column with the eluent consisting of 7.5 mmol/L NaHCO$_3$ and 1.1 mmol/L Na$_2$CO$_3$. For the analysis of IBP, the sample solution was
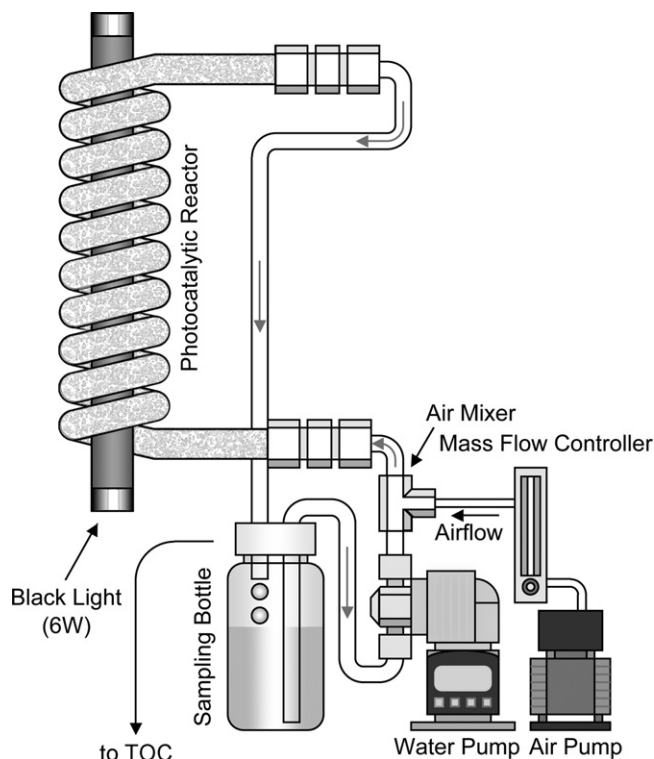

Fig. 1. Schematic of the circulation type photocatalytic reactor that was used in the study.

extracted by Sep-Pak C18 Cartridge (Waters). Low polarity compounds (including IBP) were separated by NPpak (4.6 × 250 mm) column after methanol extraction, and were observed using a L-2485 fluorescent detector. Methanol was used as eluent (Wako, HPLC grade).

Analysis of Glyphosate and AMPA was carried out by the post-column method using the above-mentioned HPLC system and a L-2485 fluorescent detector. In this method, two reactants were used. The reactants were prepared as follows: 1.4 g KH$_2$PO$_4$, 11.6 g NaCl, and 0.2 mL sodium hypochlorite were added to 800 mL of NaOH (12.5 mmol/L) solution. Reactant 1 was obtained by diluting the above solution using 1 L of water. Reactant 2 was prepared by mixing 10 mL methanol and 0.8 g o-phthalaldehyde to 800 mL of sodium tetraborate (62.5 mmol/L), diluting the mixture with 1 L of water, and then adding 2 mL of 2-mercaptoethanol to the diluted solution. The eluent was prepared by mixing 800 mL of KH$_2$PO$_4$ (25 mmol/L) with 30 mL of K$_2$HPO$_4$ (23 mmol/L) solution. Gelpack GL-IC-A27 (4.6 × 250 mm) column was used for the analysis by the post-column method.

Analysis of DEP, methylphosphonic acid, MPPA, and Glufosinate, and the detection of intermediates and final products of photocatalysis were carried out with ion chromatograph (IC: Tosoh IC-2001: column: TSKgel SuperIC-AZ, 4.6 × 150 mm; eluent: 7.5 mmol/L NaHCO$_3$ + 1.1 mmol/L Na$_2$CO$_3$). Analysis of intermediates derived from photocatalysis of IBP was carried out using HPLC with fluorescent detector (JASCO UV-2075). The sample solution was extracted by Sep-Pak C18 Cartridge (Waters), and the intermediates were separated using Devosil PAHS-5 (4.6 × 250 mm) column. The eluent used consisted of a mixture of acetonitrile: methanol: citric acid buffer (2:1:7 v/v). Some of the organophosphorus compounds such as DDVP, Monocrotophos, ESP, and DMMP was difficult to quantify using HPLC and IC, and the concentration of these chemicals was not quantified. In all cases, elimination of organophosphorus pesticides from the aqueous phase was observed based on the decrease of total organic carbon (TOC) in water.

Table 1
Name of organophosphorus compounds, their structures, molecular weights, concentration of solutions, analysis instruments, and use applications.
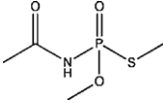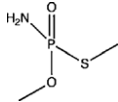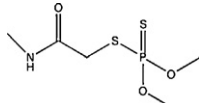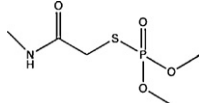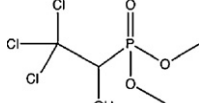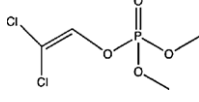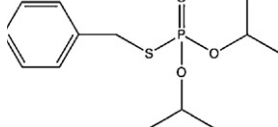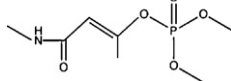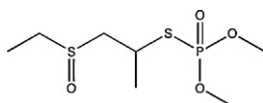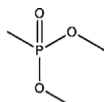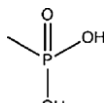
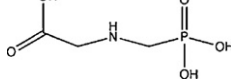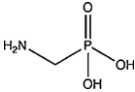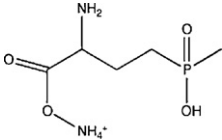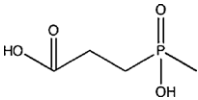| Mark in Fig. 5	Name of organophosphate (common name)	Structure	Molecular weight	Concentration of solution mol/L	Analysis Instrument (for identification of parent compound and intermediates)	Use
A	Acephate Ortran		183.2	1.09×10^{-4}	HPLC IC, TOC	Insecticide
B	Methamidophos Tamaron		141.1	1.42×10^{-4}	HPLC IC, TOC	Insecticide
C	Dimethoate Cygon		229.3	0.87×10^{-4}	HPLC IC, TOC	Insecticide
D	Omethoate Folimat		213.2	0.94×10^{-4}	HPLC IC, TOC	Insecticide
E	DEP Trichlorfon		257.4	0.77×10^{-4}	– IC, TOC	Insecticide
F	DDVP Dichlorvos		221.0	0.90×10^{-4}	– IC, TOC	Insecticide
G	IBP Kitazin-P		288.3	0.69×10^{-4}	HPLC HPLC, IC, TOC	Fungicide
H	Monocrotophos Alphate		223.2	0.89×10^{-4}	– IC, TOC	Insecticide
I	ESP Oxydeprofos		260.3	0.76×10^{-4}	HPLC IC, TOC	Insecticide
J	Dimethylmethyl Phosphonate DMMP		124.1	1.00×10^{-4}	– IC, TOC	Simulant of CWAs
K	Methylphosphonic Acid		96.0	1.00×10^{-4}	IC IC, TOC	–
L	Glyphosate		169.1	1.18×10^{-4}	HPLC[d], IC	Herbicide

Table 1 (*Continued*)

Mark in Fig. 5	Name of organophosphate (common name)	Structure	Molecular weight	Concentration of solution mol/L	Analysis Instrument (for identification of parent compound and intermediates)	Use
	Roundup				IC, TOC	
M	AMPA (Aminomethylphosphonic acid)		111.0	1.80×10^{-4}	HPLC[d] IC, TOC	Glyphosate Metabolite
N	Glufosinate Basta (Ammonium Salt)		198.2	1.01×10^{-4}	IC IC, TOC	Herbicide
O	MPPA (3-Methylphoshinico-propionic acid)		152.1	1.31×10^{-4}	IC IC, TOC	Glufosinate Metabolite

HPLC[d]: HPLC with post-column method.

In these experiments, circulation of water in the system was carried out continuously for 2 h under the dark condition and UV irradiation. Sampling for HPLC and IC analyses was performed every 15 min. TOC in the circulating solution was measured every 7 min by Shimadzu TOC-V$_{cpn}$. Changes in pH with time under the dark condition and UV irradiation were observed using a TPX-999i Toko pH meter. Initial pH of the organophosphorus solution was not adjusted to simulate actual environmental condition. As mentioned in Section 2.2, slight changes of temperature did not influence the acceleration of hydrolysis. Still, we carried out the observation of the changes of pH with slight increase of temperature as control experiment for confirmation. The UV lamp was wrapped with aluminum foil prior to irradiation. Following the start of the circulation of water, pH measurement was started, and then the aluminum foil wrapped UV lamp was turned on. The circulation time was equal to the length of the period of dark condition and UV irradiation.

3. Results and discussion

3.1. Reduction of organophosphorus compounds in an aqueous phase with photocatalysis

All of organophosphorus compounds in an aqueous phase were photocatalytically decomposed. Fig. 2 shows the changes in concentration due to the photocatalysis of Acephate as representative of organophosphorus compounds and Glyphosate as a representative of organophosphoric acids. The tendency of changes in concentration due to the photocatalysis of all organophosphorus compounds except for organophosphoric acids were very similar to Acephate, on the other hand, the tendency of changes in concentration due to the photocatalysis of all organophosphoric acids except for Glufosinate were very similar to Glyphosate. The reduction profile of the parent compounds under dark condition was completely different between organophosphoric acids and other organophosphorus compounds. That is to say, organophosphoric acids drastically decreased right after the solutions were circulated into the reactor, and no significant decrease in the concentration of the other organophosphorus compounds was observed under the dark condition.
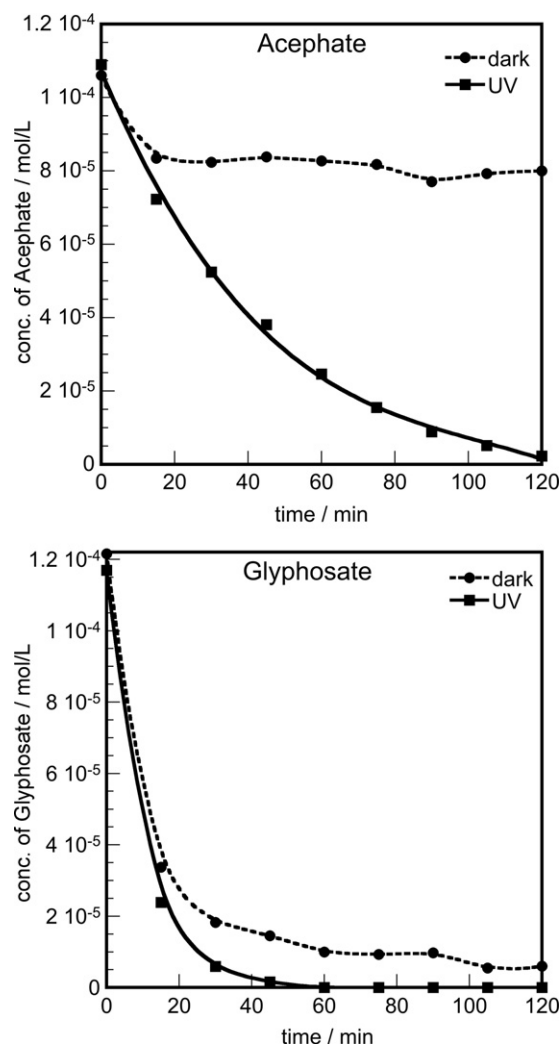

Fig. 2. Changes in the concentration of Acephate and Glyphosate under the dark condition and UV irradiation for 2 h.

Table 2
Rate constant of photodegradation of organophosphorus compounds.

Compounds	Acephate	Methamidophos	Dimethoate	Omethoate	DEP	IBP
Rate constant K	0.0253	0.0129	0.0904	0.0481	0.0585	0.0213

It is clear that all of organophosphorus compounds were simply decreased with UV irradiation. In particular, the profile of photodegradation kinetics of organophosphorus compounds other than organophosphoric acids seems pseudo first-order. Calculation of apparent rate constant, k, was simply obtained from Eq. (1),

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{1}$$

where C_0 and C are initial and actual concentration of organophosphorus compounds other than organophosphoric acids respectively. Under the assumption as pseudo first-order kinetics, the rate constant k of photodegradation of organophosphorus compounds except for organophosphoric acids were shown in Table 2. On the other hand, except for Glufosinate, the significant difference in the decrease of organophosphoric acids between the dark condition and UV irradiation was not observed. In this work, we used Glufosinate ammonium salt. We propose that this ammonium salt inhibited the adsorption of Glufosinate onto TiO_2 surface. Myller et al. found that while P—O—Ti bonds did not form in their study using inorganic $(NH_4)_3PO_4$ [41]. However, in our case, the reason of no formation of Ti—O—P bonds is just speculation from the experimental results of abnormal behavior of Glufosinate ammonium salt different from general organophosphoric acids. If we need to provide the evidence of no formation of Ti—O—P bonds, we should observe the surface of TiO_2 by FT-IR [42].

3.2. Changes of TOC with photocatalysis of organophosphorus compounds

Changes of TOC in an aqueous phase containing Acephate, as representative of organophosphorus compounds, under the dark condition and UV irradiation are shown in Fig. 3, while that for Glyphosate, as representative of organophosphoric acids, is shown in Fig. 4. Table 3 shows the changes of actual TOC value and changes % of all organophosphorus compounds under the dark and UV irradiation. The decrease of TOC profile of Acephate as shown in Fig. 3 and the other organophosphorus compounds as shown in Table 3
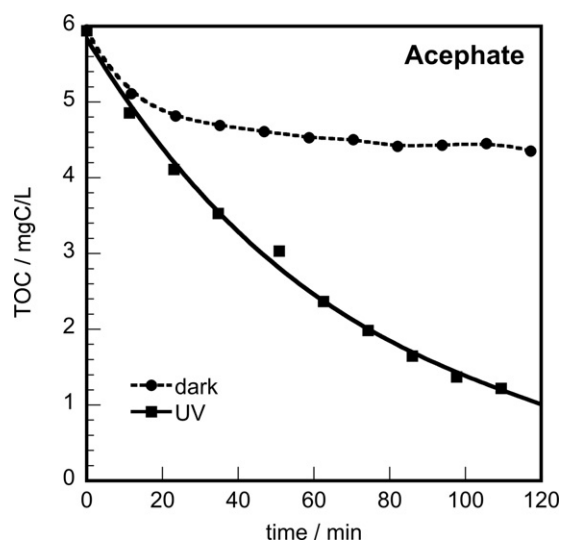
is very similar to the result of photocatalytic degradation of it as shown in Fig. 2. On the other hand, the decrease in the TOC profile of the Glyphosate solution as shown in Fig. 4 and the other organophosphoric acids except for Glufosinate as shown in Table 3 is different from that of Fig. 2 under UV irradiation. That is to say, the TOC level of organophosphoric acid solutions was drastically decreased with the adsorption of itself onto TiO_2 surface under the dark condition. On the other hand, TOC level of organophosphoric acids (except for Glufosinate) under UV irradiation was higher than in the dark condition. It is difficult to determine whether the decrease of organophosphoric acid under UV irradiation was depended on a photocatalysis or adsorption from the result of Fig. 2 alone. However, based on TOC results, the initial decrease in the concentration of organophosphoric acids seems to result from the adsorption of the compounds on TiO_2 surface. Upon continuous UV irradiation, the adsorbed organophosphoric acids were photocatalytically decomposed into various organic intermediates and CO_2 that eluted into the aqueous phase, leading to an increase in TOC levels that are higher than that obtained under dark condition as shown in Table 3. To confirm this speculation, formation of intermediates during photocatalytic reaction was evaluated as discussed in the next section.

3.3. Formation of intermediates and final products with photocatalysis of organophosphorus compounds

Fig. 5 shows the time course of the formation of intermediates and final products with photocatalysis of organophosphorus compounds. The plausible photocatalysis schemes of organophosphorus compounds based on the result of intermediates and final products formation were proposed. In all cases, photocatalysis of organophosphorus compounds resulted in the formation of formic acid that initially increased with UV irradiation, but eventually decreased with the progress of photocatalytic reaction. Acetic acid, maleic acid, and other organic acids, which show similar profile as formic acid, were also detected during UV irradiation. Apart from organic acids, formation of inorganic intermediates

Fig. 3. Changes in the total organic carbon (TOC) concentration of aqueous solutions of Acephate under the dark condition and UV irradiation for 2 h.
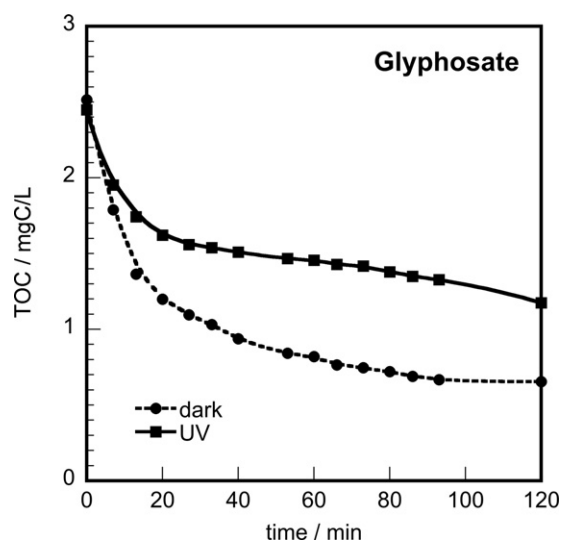

Fig. 4. Changes in the total organic carbon (TOC) concentration of aqueous solutions of Glyphosate under the dark condition and UV irradiation for 2 h.

Table 3
TOC analysis of organophosphorus solution under the dark condition and UV irradiation.

Mark in Figs. 5 and 7	Name of organophosphate	Expected conc. (mgC/L)	Ini. conc. → conc. after 2 h under dark (mgC/L)	Ini. conc. → conc. after 2 h under UV (mgC/L)	Reduction rate %/2 h under dark	Reduction rate %/2 h under UV
A	Acephate	5.23	5.95 → 4.35	5.94 → 1.01	26.9	83.0
B	Methamidophos	3.41	3.04 → 1.87	3.04 → 0.36	38.5	88.2
C	Dimethoate	5.22	5.75 → 4.04	5.88 → 1.20	29.7	79.6
D	Omethoate	5.64	6.06 → 4.64	5.62 → 1.05	23.4	81.3
E	DEP	3.70	3.76 → 3.12	3.81 → 0.00	17.0	100.0
F	DDVP	4.32	4.22 → 1.51	4.33 → 0.04	64.2	99.1
G	IBP	10.76	9.76 → 7.37	9.76 → 0.95	24.5	90.3
H	Monocrotophos	7.48	7.57 → 5.73	7.54 → 0.50	24.3	93.4
I	ESP	6.38	6.95 → 4.85	6.97 → 0.50	30.2	92.8
J	DMMP	3.60	3.87 → 3.27	3.83 → 0.80	15.5	79.1
K	Methylphosphonic acid	1.20	1.39 → 0.18	1.37 → 0.10	87.1	92.7
L	Glyphosate	4.25	2.52 → 0.65	2.45 → 1.18	74.2	51.8
M	AMPA	2.16	2.37 → 0.00	2.41 → 0.00	100.0	100.0
N	Glufosinate (Ammonium Salt)	6.06	7.24 → 4.55	7.09 → 1.85	37.2	73.9
O	MPPA	6.29	6.46 → 0.58	6.60 → 0.00	91.0	100.0
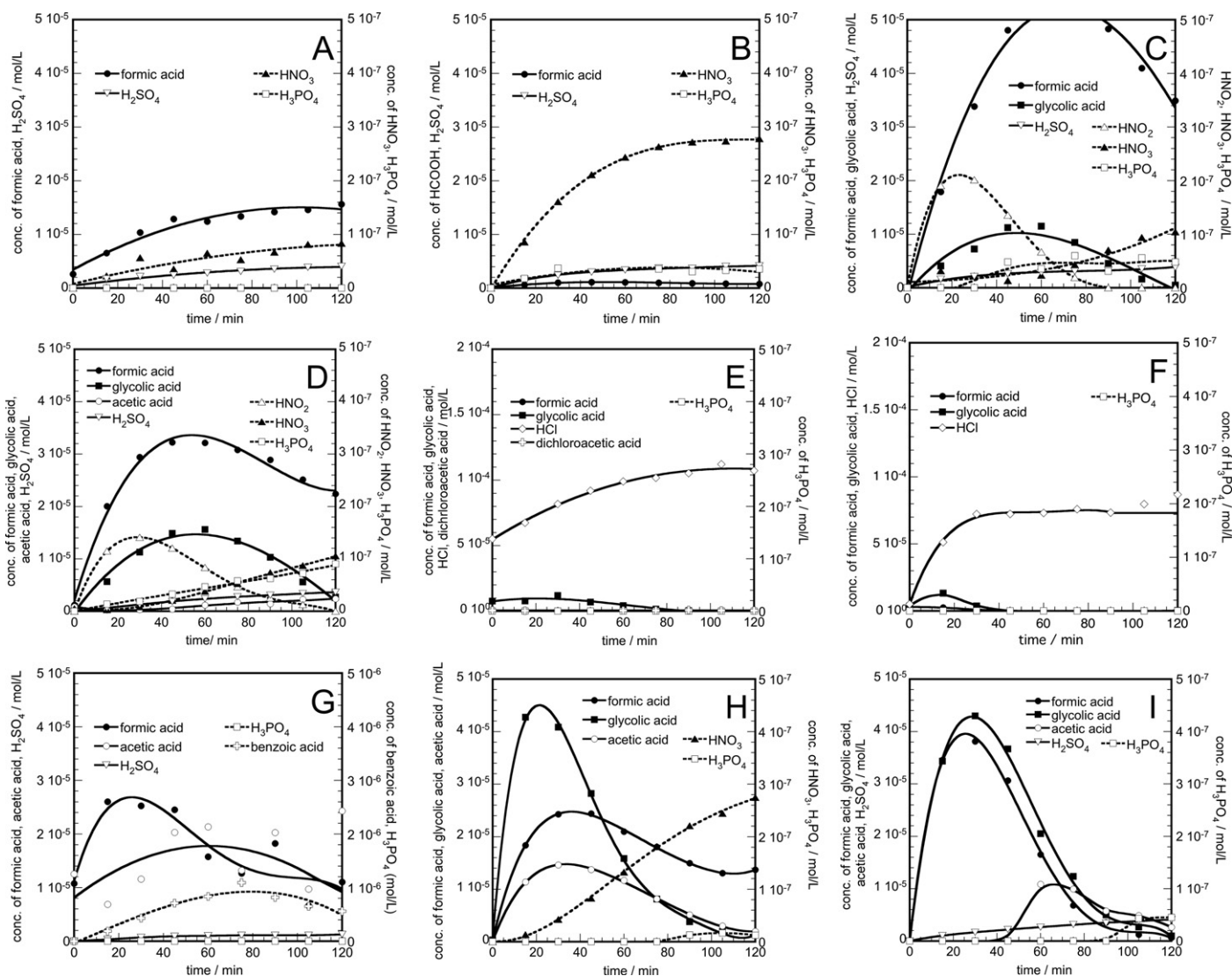
Fig. 5. Time course of the formation of intermediates and final products during the 2 h photocatalysis of organophosphorus compounds. A: Acephate, B: Methamidophos, C: Dimethoate, D: Omethoate, E: DEP, F: DDVP, G: IBP, H: Monocrotophos, I: ESP, J: DMMP, K: methylphosphonic acid, L: Glyphosate, M: AMPA, N: Glufosinate, O: MPPA.
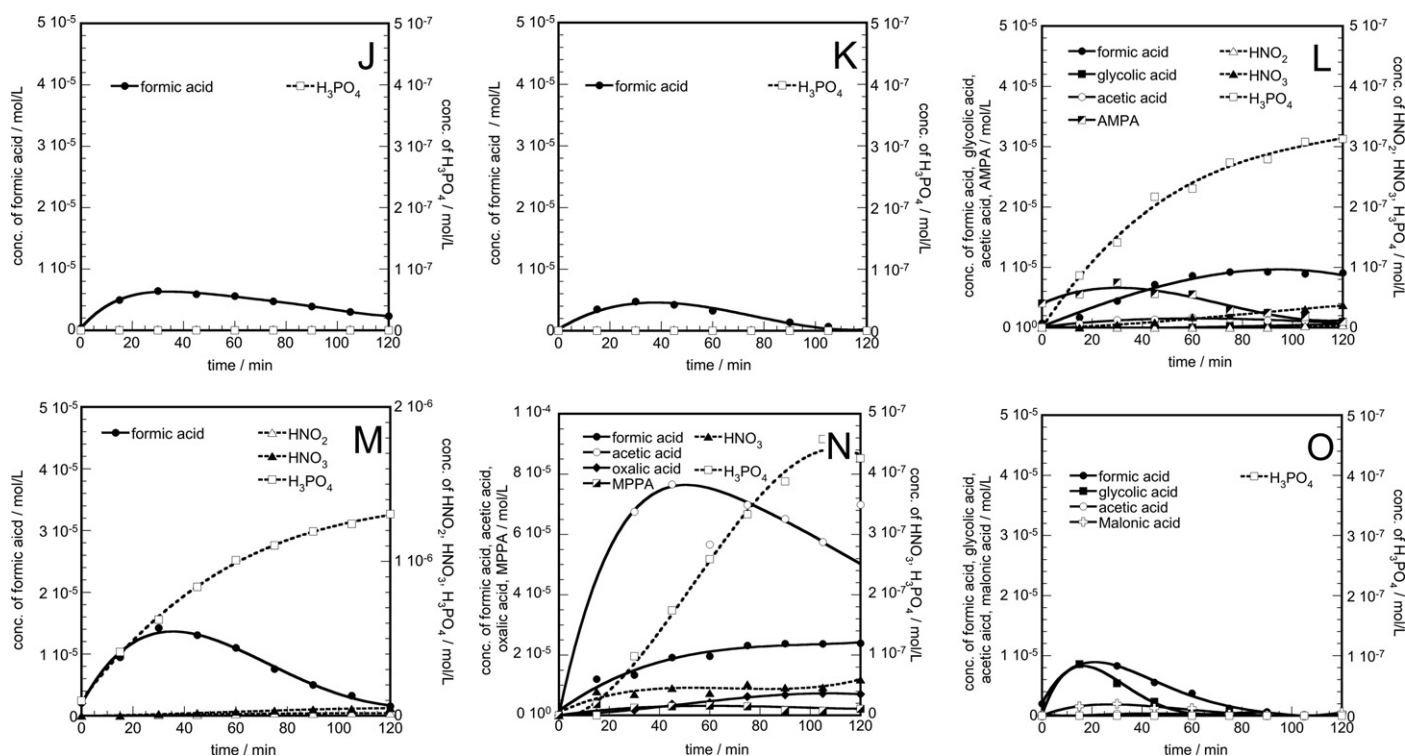
Fig. 5. (*Continued*)

was also observed. For instance, nitrogen-containing organophosphorus compounds such as Dimethoate (Fig. 5C) and Omethoate (Fig. 5D) generate HNO_2 and HNO_3. Initially, the concentration of HNO_2 increased and then decreased with UV irradiation, while formation and accumulation of HNO_3 appear to coincide with the decrease of HNO_2. On the other hand, formation of HNO_2 was not observed with the photodegradation of Acephate and Methamidophos. They are typical phosphoramidates, and direct formation of HNO_3 may be related with the timing of the cleavage of P–N bond. H_2SO_4 was increased with photocatalysis of sulfur-containing compounds such as Acephate, Methamidophos, Dimethoate, Omethoate, IBP, and ESP. With the photodegradation of DEP and DDVP, which are chlorine-containing organophosphorus, formation of HCl was observed. Formation of dichloroacetic acid was observed with photocatalysis of DEP. However, this compound was slightly decreased during 2 h UV irradiation. It is known that the photodegradation of dichloroacetic acid is little difficult to decompose by naked TiO_2 photocatalyst. Complete decomposition of DEP was reported to be possible only by using Pt-loaded TiO_2 photocatalyst [43,44].

The most characteristic thing in our study is that the photodegradation of organophosphorus compounds at around 1×10^{-4} mol/L solution was completed within 2 h under UV irradiation, and formation of H_3PO_4 was not observed or was barely detectable after 2 h photocatalysis. An exception is the case of Glyphosate, AMPA, and Glufosinate. With the photodegradation of Glyphosate, formation of H_3PO_4 was observed as reported [37]; this final product was also observed with photodegradation of AMPA and Glufosinate.

It has been reported that Acephate, Dimethoate, Glyphosate, and Glufosinate are hydrolyzed into Methamidophos [45–47], Omethoate [19], AMPA [21,48,49], and MPPA [50–52], respectively. The photocatalysis route of these organophosphorus compounds will be expected if these intermediates similar to those formed by hydrolysis with photocatalysis are not observed in an aqueous phase. Han et al. [45] qualitatively observed the formation of

Methamidophos derived from the photocatalysis of Acephate by GC–MS. However, we did not detect the formation of Methamidophos with photocatalysis of Acephate at around 1×10^{-4} mol/L by HPLC. Similarly, formation of Omethoate derived from photocatalysis of Dimethoate was under the detection limit of HPLC. On the other hand, small amount of AMPA was observed with the photocatalysis of Glyphosate by HPLC (Fig. 5L). Trace level of MPPA formation was observed with the photocatalysis of Glufosinate (Fig. 5N). However, it is expected that these organophosphoric intermediates were continuously photodecomposed with progress of UV irradiation. It is considered that the elution of organophosphoric intermediates and H_3PO_4 into aqueous phase with photocatalysis of organophosphorus compounds is related to the strength of interaction between the surface of TiO_2 and these phosphoric acids. Similar to phosphates, it is expected that sulfates and nitrates also adsorb onto TiO_2 surface. However, the interaction between these inorganic compounds and TiO_2 is smaller than phosphates, therefore, elution of sulfates and nitrates were observed in the early stage of UV irradiation.

The results of IC analysis show formation of organic acids as intermediates of the photocatalysis of organophosphorus compounds. As shown in Fig. 3 and Table 3, the total amount of these intermediates was smaller than that of the initial TOC. We expect that the organophosphorus compounds were photooxidized to organophosphoric acids that were, in turn, rapidly adsorbed onto TiO_2 surface. These adsorbed organophosphoric acids, including some of the organic functional groups, were afterward photooxidized to CO_2. Thus, the total amount of organic acids observed was lower than that of TOC results.

3.4. Changes of pH with photocatalysis of organophosphorus compounds

Changes in the pH profile during photocatalysis of organophosphorus compounds other than organophosphoric acids were different from that of organophosphoric acids. Changes in pH

Table 4
Changes of pH after UV irradiation.

Compounds	Acephate	Methamidophos	Dimethoate	Omethoate	Glyphosate	AMPA	Glufosinate	MPPA
pH in dark	4.59	4.83	5.67	4.64	4.90	6.12	5.13	4.74
pH under UV	4.21	4.75	5.03	4.50	4.84	5.83	5.25	4.65
Difference	−0.38	−0.08	−0.64	−0.14	−0.06	−0.29	+0.12	−0.09

Table 5
Changes of pH and their ratio of change with photoirradiation.

	Acephate	Methamidophos	Dimethoate	Omethoate	Glyphosate	AMPA	Glufosinate	MPPA
Dark	4.63	4.89	5.84	4.76	4.87	6.01	5.22	4.71
UV	4.18	4.80	5.02	4.49	4.8	5.87	5.26	4.66
Difference	0.45	0.09	0.82	0.27	0.07	0.14	−0.04	0.05
%	3.2	0.7	5.9	1.9	0.5	1.0	0.3	0.4

with photodegradation of Acephate and Glyphosate are shown in Fig. 6 as the representative of organophosphorus compounds and organophosphoric acid respectively. On the other hand, changes in pH with photodegradation of Acephate, Methamidophos, Dimethoate, Omethoate, Glyphosate, AMPA, Glufosinate,
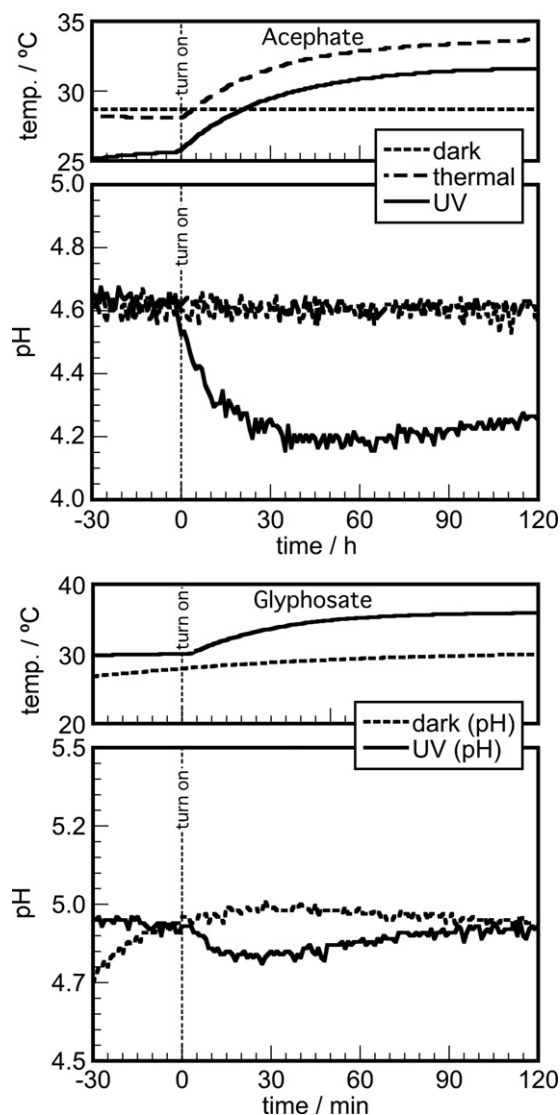

Fig. 6. Changes in pH and in temperature of aqueous phase during the 2 h photocatalysis of Acephate and Glyphosate.

and MPPA are shown in Table 4. The pH of the organophosphorus solutions drastically decreased upon UV irradiation, whereas, only a small shift in pH occurs in the case of organophosphoric acids (Table 4). Here, the observed slight decrease in pH under the dark condition can be related to the dissolution of CO_2 from the air bubbling procedure that was confirmed in an experiment using distilled water. Normally, the rapid drop in pH upon UV irradiation results from the formation of organic acids as intermediates and of inorganic acids and CO_2 as final products during photocatalysis [53]. However, in this study, pH was slightly increased with progress of photocatalysis. This result shows that organic acids as intermediates were re-oxidized by the photocatalyst. For example, during the photocatalytic decomposition of Dimethoate, the concentration of formic acid and glycolic acid reached their maximum after 60 min UV irradiation and continuously decreased, thereafter (Fig. 5 C). This result is consistent with the profile of pH changes shown in Table 4. This behavior was also observed in the photocatalysis of the other organophosphorus compounds (Table 5).

Since the photocatalytic reactor used involved a closed circulation system, it was expected that the temperature inside the photocatalytic reactor would increase with UV irradiation. To determine the possible influence of the increase in temperature on the degradation, particularly on the hydrolysis of organophosphorus compounds, its effect on the pH of solutions was determined. The time course of pH changes with temperature during the photocatalysis of Acephate is shown in Fig. 6. It can be noted that temperature increase (that peaks at around 5 °C) did not result in significant changes in the pH of Acephate solution. In fact, it was found that the pH profile of Acephate solution under UV irradiation almost overlaps with that of the dark condition. As this behavior has also been observed in the photocatalysis of the other organophosphorus compounds, the effect of the slight temperature increase on the hydrolysis of organophosphorus compounds is therefore considered negligible.

It is known that the changes of reaction rate for photocatalysis of organophosphorus compounds depend on the initial pH [54]. However, our research work focused on the simulation of the photocatalytic degradation of organophosphorus compounds in an actual environmental condition [55], and the influence of initial pH changes on the reaction rate was not investigated in this study. Connor and McQuillan [56] reported that the adsorption efficiency of phosphoric acid onto TiO_2 depends on pH, that is, the interaction between phosphoric acid and TiO_2 increases as pH decreases with a threshold at around pH 6. In our experiments, the initial pH of the organophosphorus solution was acidic and except for some organophosphoric acids, pH was found to decrease with UV irradiation. Thus, except for organophosphoric acids, little or no elution of phosphoric acid was observed during the photodegradation of the organophosphorus compounds.
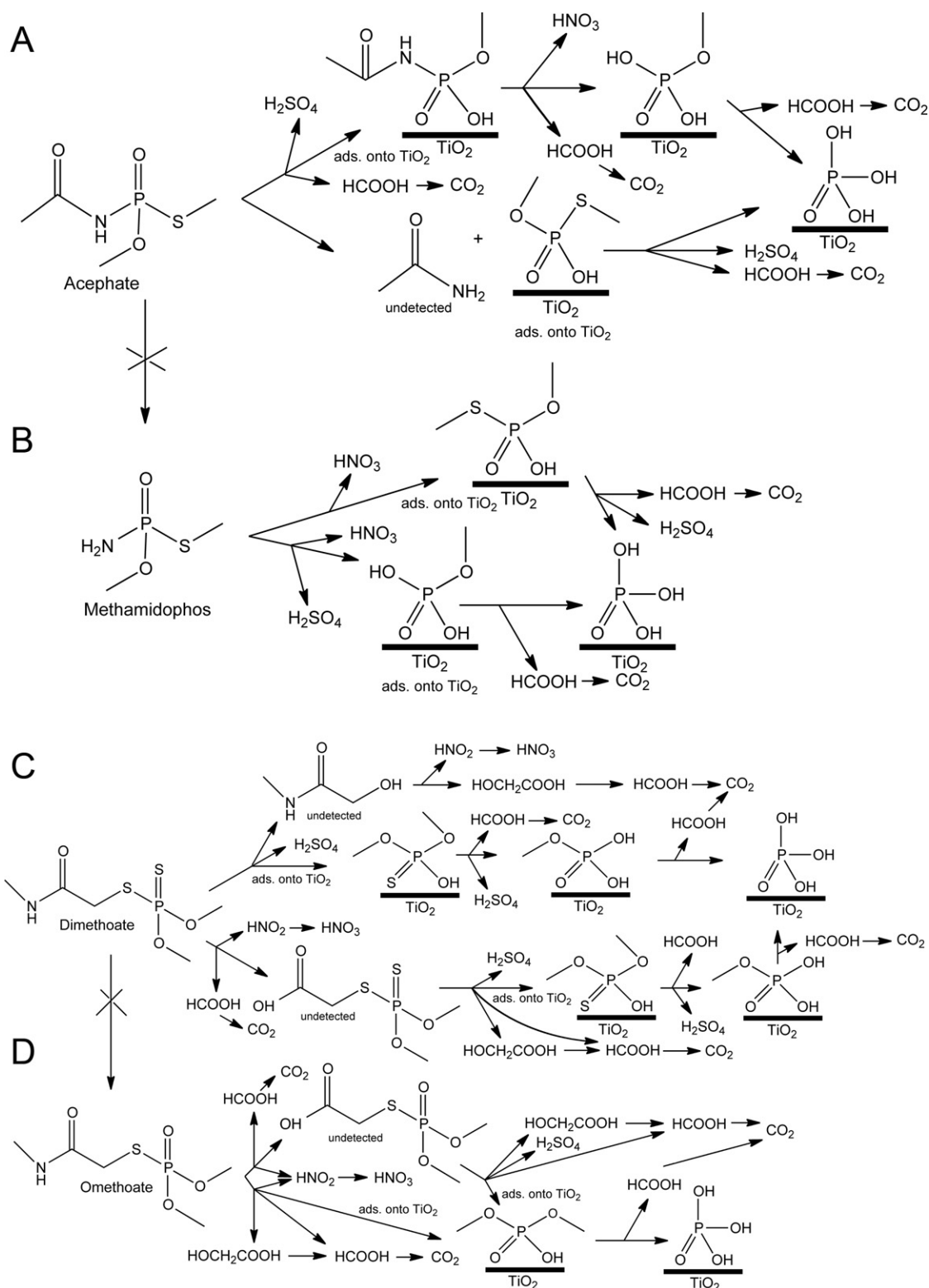
Fig. 7. Expected photodegradation scheme of organophosphorus compounds. A: Acephate, B: Methamidophos, C: Dimethoate, D: Omethoate, E: DEP, F: DDVP, G: IBP, H: Monocrotophos, I: ESP, J: DMMP, K: methylphosphonic acid, L: Glyphosate, M: AMPA, N: Glufosinate, O: MPPA.

As for the organophosphoric acids, only small changes in pH with UV irradiation were observed. This result likely indicates the state at which the rate of degradation of parent organophosphorus compounds is equal to the rate of formation of organic and inorganic intermediates and final products during the 2 h UV irradiation. Nevertheless, photocatalytic degradation of all organophosphorus compounds progressed under low pH conditions throughout the experiment. It is considered, however, that the pH condition is not responsible for desorption of phosphoric acid from Glyphosate, AMPA, and Glufosinate.
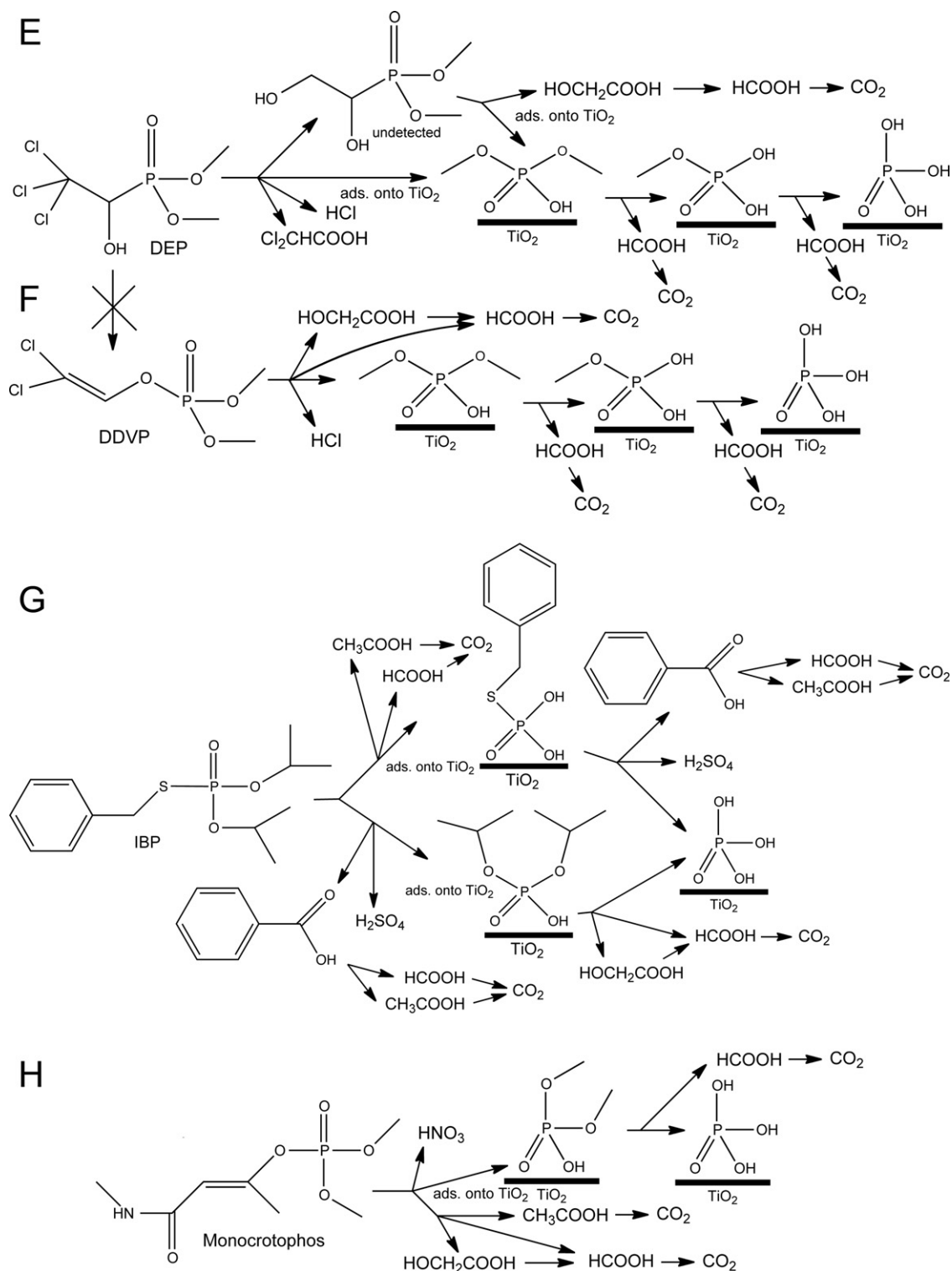
Fig. 7. (Continued)

3.5. Proposed degradation pathway of organophosphorus compounds

The detailed analysis of the formation mechanism of active species on the TiO$_2$ surface during the photocatalysis of organic compounds such as organophosphorus compounds has already been reported elsewhere [4,5,14,55,57–59]. Basically, it is considered that the photocatalysis mechanism of organophosphorus compounds by active species such as active oxygen or hydroxy radical is not different from that of other organic compounds. However, debates are still on-going concerning on which atomic bond in organophosphorus molecules does photocatalytic cleavage occurs. As for Acephate and Methamidophos, it is considered that P−N bond cleavage did not occur preferentially at the initial stage of photocatalysis compared to the cleavage of the other bonds [43,60]. Han et al. [45] reported that the cleavage of N−C bond

Fig. 7. (*Continued*)
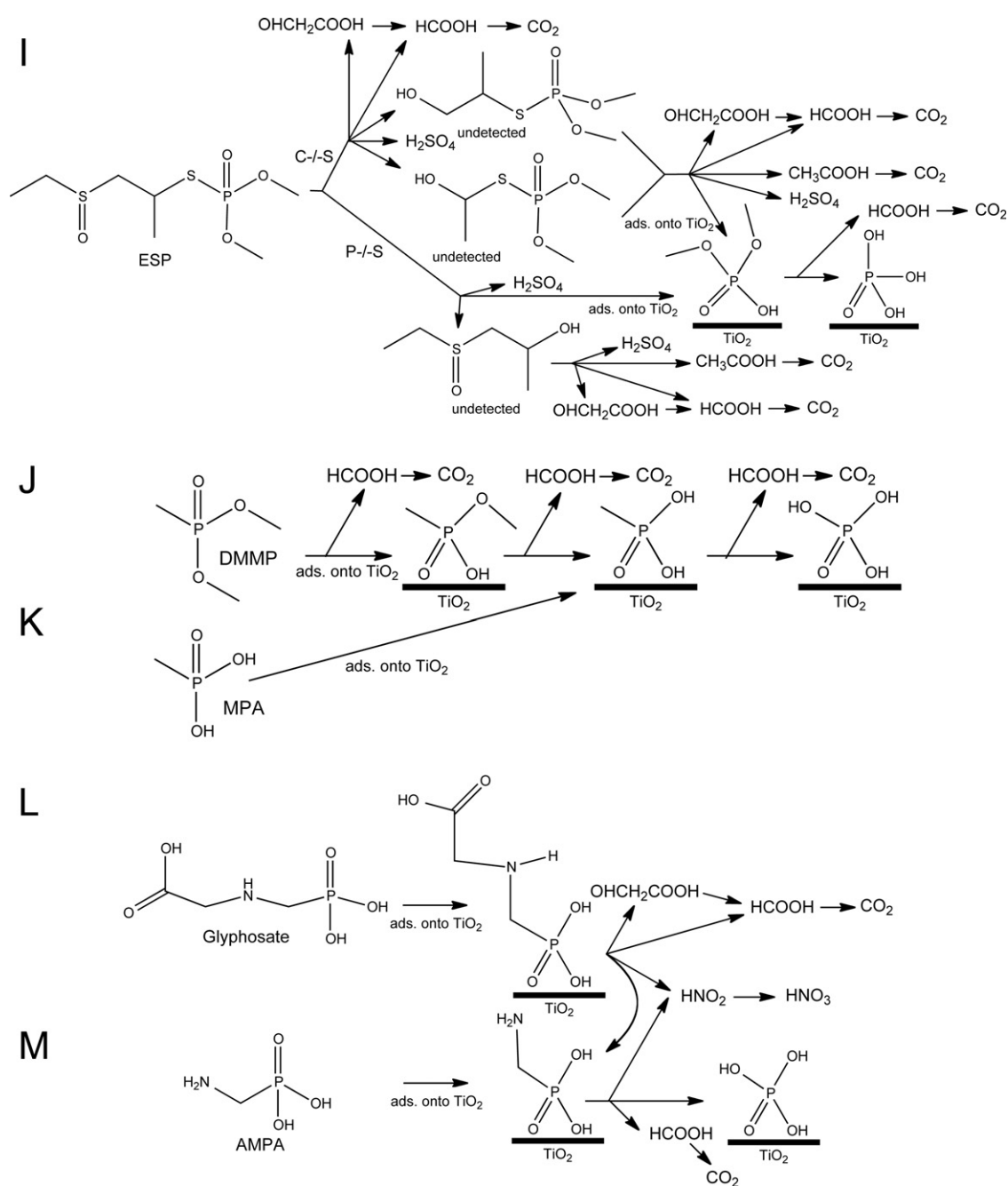
occurred initially, and then P—N and C—C oxidative cleavage proceeded subsequently. However, if the cleavage of N—C bond did occur, formation of Methamidophos would have been observed. Likewise, acetic acid and glycolic acid would have been formed with the cleavage of the N—C bond. But as shown in Fig. 5 A, we did not observe the above intermediates, and we supposed that the possibility of the initial N—C cleavage is low. Similar to the study reported by Rahman et al. [61], we propose that initially, the acetyl group in Acephate underwent oxidation, followed by elimination of —SCH$_3$ or —OCH$_3$ and subsequent formation of organophosphoric acid that was adsorbed onto TiO$_2$ surface. However, as the results indicate, the photocatalytic degradation of Acephate is slow, and the conversion of organophosphorus compound to organophosphoric acid is the rate-determining step in the process. Photocatalysis of Methamidophos, on the other hand, was

even slower than Acephate, which is consistent with the results of Han et al [45]. Based on the results of this study, it appears that degradation of Acephate does not involve formation of highly toxic Methamidophos (Fig. 7A) as what happens during hydrolysis of Acephate. This finding is of particular importance in the photocatalytic treatment of pesticide-contaminated water.

In the case of Dimethoate and Omethoate, the position of bond cleavage with photocatalysis does not only involve P—S bond but also S—C bond cleavage [19]. In this study, it was found that similar to Acephate, the photocatalytic degradation route of Dimethoate does not go through the hydrolysis pathway, which involves formation of Omethoate. Therefore, it is proposed that P-S bond cleavage predominates in the early stage of the photocatalysis of Dimethoate. Evgenidou et al. [19] described that the preferential cleavage of P=S or P—S bond in Dimethoate depends on a
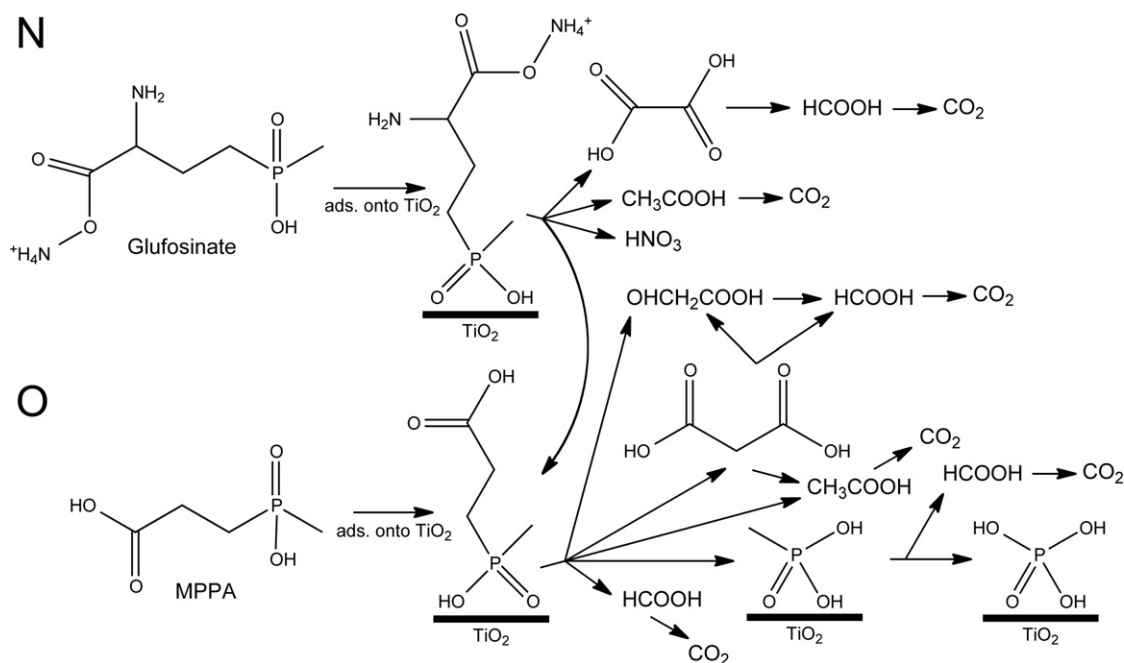
Fig. 7. (*Continued*).

contribution of OH• or h⁺. In our study, the formation of Omethoate derived from the photocatalysis of Dimethoate was not observed. Therefore, it is thought that P—S bond cleavage dominates in the early stage of photocatalysis. On the other hand, it is expected that the cleavage of C—N bond will occur when the contribution of h⁺ is high. We also observed the formation of HNO_2 in the early stage of photocatalysis, and as a result, we considered that the cleavage of C—N bond occurred. The proposed scheme for the degradation of Dimethoate and Omethoate are shown in Fig. 7C and D, respectively.

It is known that DEP is decomposed through DDVP by hydrolysis. But since we did not determine the quantity of intermediates, we could not directly propose the route of photocatalysis of DEP. However, we found the formation of dichloroacetic acid with photocatalysis of DEP in this study but not during the decomposition of DDVP. From this result, we conclude that the degradation scheme of DEP by photocatalysis is different from the hydrolysis route. The expected scheme for the photocatalysis of DEP and DDVP are shown in Fig. 7E and F, respectively.

The proposed photocatalytic degradation path of IBP is consistent with that described by Wen et al. [62]. Cleavage of C—S bond occurred in the early stage of photocatalysis, leading to the formation of benzoic acid as shown in Fig. 7G. It is considered that the photocatalysis route of IBP after formation of benzoic acid was almost similar to the photocatalytic degradation pathway of the other organophosphorus compounds.

In the case of Monocrotophos photodegradation, it is considered that active species attack the double bond (C=C) in Monocrotophos [63,64]. The photocatalytic degradation scheme of Monocrotophos was easy to estimate because similar to the findings of Chen et al. [65], all of the expected organic acids intermediates were observed. Our expected scheme for the photocatalysis of Monocrotophos is shown in Fig. 7H.

We could not find any reference on the degradation of ESP in the literature. However, it is considered that the basic route of the photocatalytic degradation of ESP may be similar to the photocatalysis mechanism of the other organophosphorus compounds. Formation of glycolic acid was observed at the early stage of ESP degradation. With prolonged reaction time, acetic acid was continuously

generated (Fig. 5I). It is proposed that the photocatalysis of ESP results in the oxidation of the methoxy group that is bound to P, into hydroxy group. However, since a remarkable decrease in TOC after UV irradiation was not observed, it is possible that the organic intermediates were adsorbed onto TiO_2 surface and that the oxidation of methoxy group is not dominant in this scheme. Similar to the photodegradation of Acephate and Methamidophos, we also observed the formation of H_2SO_4 at the early stage of photocatalysis. Thus, it is considered that P—S or C—S bond cleavage occurred at the initial stage of photocatalysis and that the organic acids continually decreased with the progress of UV irradiation. The expected scheme of photocatalysis of ESP is shown in Fig. 7I.

Since the chemical structure of DMMP is simple, its photocatalytic degradation scheme is also easy to determine. The expected organic intermediate is formic acid only, which may have likely initially result from the rapid oxidation of formaldehyde [66]. It is probable that dimethylphosphinic acid was formed from DMMP oxidation, and was adsorbed onto TiO_2 surface immediately (Fig. 7J). This dimethylphosphinic acid was oxidized on TiO_2 surface and re-oxidized to methylphosphonic acid (Fig. 7K), and finally oxidized into H_3PO_4. However, H_3PO_4 was not observed in the aqueous phase during the 2 h UV irradiation, suggesting adsorption of this final product on TiO_2 surface. It is considered that the adsorption mechanism of the photodegradation of DMMP is directly applied to the decontamination of chemical warfare such as Sarin. That is to say, cleavage of P—F bond in Sarin is induced by photocatalysis, continuously formed isopropyl methylphosphonate will be immediately adsorbed onto TiO_2 surface. Therefore, it is expected that the toxic main body will be immediately removed from the aqueous phase by photocatalytic reaction [67,68].

It is found in this study that the photocatalytic degradation scheme of organophosphoric acids is different from the other organophosphorus compounds and that these acids are rapidly and strongly adsorbed onto TiO_2 surface in aqueous phase. Upon UV irradiation, C—H and C—C bonds in organophosphoric acids are gradually cleaved and intermediates such as organic acids are eluted into the aqueous phase. During the photocatalytic degradation of methylphosphonic acid, the expected final product H_3PO_4 was not observed, indicating adsorption of H_3PO_4 onto TiO_2 surface

after the photocatalytic decomposition of the parent compound. The photocatalysis scheme of methylphosphonic acid is illustrated in Fig. 7K.

Glyphosate and its metabolite, AMPA, were found to strongly adsorb onto TiO_2 surface in aqueous phase (Fig. 2). The results show that photocatalysis of organophosphoric acids results in forms organic acids as intermediates and inorganic acids as final products. However, unlike the other organophosphorus compounds described earlier, elution of H_3PO_4 into the aqueous phase was observed. It is thought that elution of H_3PO_4 may depend on the difference of interaction between organophosphoric acids and H_3PO_4 with the TiO_2 surface. For instance, it is supposed that Glyphosate and AMPA, which are strongly adsorbed onto TiO_2 surface, are continuously decomposed into H_3PO_4 by photocatalysis. Since not only H_3PO_4 but also AMPA were eluted into the solution during Glyphosate photocatalysis, it is considered that Glyphosate is converted into AMPA that has lower affinity for TiO_2. The elution mechanism of AMPA into the aqueous phase is similar to that of H_3PO_4 [54].

As for Glufosinate, MPPA was found as an intermediate and H_3PO_4 as the final product of the photocatalysis. Similar to Glyphosate, photocatalytic decomposition of Glufosinate generates MPPA that was then immediately adsorbed onto TiO_2 and then competed with Glufosinate for adsorption sites. In the case of MPPA, H_3PO_4 as final product was not observed during photocatalysis as shown in Fig. 5O. One possible reason is that Glufosinate ammonium salt, and NH_4^+ act as inhibitors of anion adsorption onto TiO_2 surface. However, additional research is needed to better understand and elucidate the photocatalytic degradation scheme of Glufosinate. While Glufosinate is a widely used general herbicide, there have been very few research work conducted on the photocatalytic detoxification of this compound [50].

4. Conclusion

Various kinds of water-soluble organophosphorus compounds were effectively photooxidized by TiO_2 immobilized photocatalyst. In addition, toxic intermediates such as organophosphoric acids did not elute into the aqueous phase, indicating that the oxidized organophosphorus compounds were adsorbed onto TiO_2 surface as organophosphoric acids. This decomposition characteristic is different from that of hydrolysis. Initially, the organophosphoric acids were adsorbed onto TiO_2 surface, resulting in a significant decrease in their concentration even before UV irradiation. Upon UV irradiation, the adsorbed organophosphoric acids were photooxidized leading to the formation of organic intermediates that elute into the aqueous phase and caused the increase in TOC concentration at levels that are higher than that in the dark condition. In addition, the final byproduct H_3PO_4, was also adsorbed on TiO_2 making it difficult to detect in aqueous solutions. Elution of H_3PO_4 is considered to depend on the strength of interaction between the organophosphoric acids and TiO_2. For instance, it is assumed that H_3PO_4 will be eluted to the aqueous phase when another compound that has a higher affinity with TiO_2 is present.

Acknowledgements

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